Glass-metal composites with graded interface by potential-enhanced shaping

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Glass–metal composites find a wide range of application in illumination engineering and microelectronics. By means of potential-assisted deposition techniques glass-metal junctions with adjustably graded chemical composition can be produced. Intrinsic problems of common manufacturing technologies, like generation of high residual stresses near the sharp interface, can thus be minimised. Such composites can be prepared by means of electrophoretic or electrolytic deposition of a metal oxide or metal respectively within the open pores a silica glass green body and subsequent sintering of the green composite. Extension and steepness of the gradient (measured by EDX and optical spectroscopy) could be controlled by adjusting the process parameters during impregnation and by tailoring green density and pore structure of the silica glass green body, which was prepared by electrophoretic deposition.

Introduction

Glass metal junctions play an important role either in lighting engineering as in microelectronics. In conventional joining technique a discontinuous glass metal junction with a sharp interface is achieved. Above transformation, at suitable viscosity, the glass is squeezed onto the metal. Subsequently the glass metal composite is cooled down to room temperature. Due to the highly incompatible mechanical and thermo-physical properties of glasses (especially silica glass) and metals (e.g. α_{th}(tungsten) = $4.6 \cdot 10^{-6}$ 1/K, α_{th}(silica glass) = $0.5 \cdot 10^{-6}$ 1/K) high residual stresses can arise during joining that cannot be disregarded. Conventionally these residual stresses are partly compensated by using one ore more sealing glasses that are applied onto the metal layer-wise[i,ii]. Due to a gradual change in thermal expansion coefficient of these sealing glasses a stepwise adjustment of the thermal expansion from metal to mantle glass and hence a reduction of residual stresses is achieved. But not only thermal expansion is a key factor that has to taken into account but also strength of adhesion between sealing glass and metal, which in turn is determined by wetting behaviour and chemical interaction, plays an important role[iii]. The necessity to apply several sealing glasses much complicates the manufacturing process of glass metal types in conventional production technology. Furthermore, as a consequence of a proceeding miniaturisation of lighting components and microelectronic parts very small tolerance have to be kept. This becomes increasingly difficult with common joining of glasses to metal. Furthermore, in lighting manufacturing centre of metallic mandrel or current lead becomes more and more difficult with miniaturisation.

An alternative for the minimisation of residual stresses in glass metal composites and for an enhanced manufacturing of small components with glass-metal junction lies in the powder technological manufacturing of glass-metal composites with functionally graded composition. Due to the large specific surface area between metal and glass phase mismatch of the thermo-physical properties of glass and metal can be compensated, if an appropriate gradient is prepared[iv]. Thus, residual stresses can be minimised[v].

Electrophoretic deposition (EPD) is a shaping process for ceramics and glasses that has an outstanding suitability for the deposition of nanosized particles. In case of EPD deposition rate is independent of particle size in contrast to slip or pressure casting e.g. This enables a

fast and cost-efficient forming of glass and especially silica glass components from nanosized fumed silica particles[vi] or mixtures of smaller and coarser particles. It is important to minimise sintering temperature in powder manufacturing of silica glasses in order to avoid crystallisation. This can be achieved by using nanosized powders were sintering temperatures from 1450 to 1250 °C are reached (e.g. Degussa Aerosil OX50, A380). But even for powder mixtures of some nanosized and coarser particles sintering temperatures are sufficiently low (1500 to 1550 °C) to avoid crystallisation in particular because crystallisation velocity is very low in case of pure silica glass. Further advantages of the electrophoretic deposition from aqueous suspensions as shaping technique are high deposition rates, low energy-input and good environmental compatibility. A silica green body with a thickness of e.g. 10 mm can be obtained after less than 5 minutes deposition time with an applied electric field of 5 V/cm[vii]. Comprehensive reviews about electrophoretic deposition as coating and shaping technique for ceramics and glasses can be found in[viii, ix]

Experimental set-up

Silica green bodies were prepared by electrophoretic deposition of silica particles from aqueous suspensions. Silica powders of different particle size distribution were dispersed gradually in bidistilled water by means of a Dissolver (PC Laborsysteme) under constant applied torque. Vacuum was applied to avoid incorporation of air bubbles into the suspension. Nanosized fumed silica particles with a mean particle size of 8 to 40 nm respectively (Degussa Aerosil A380, OX50) were used as well as coarser silica powders and mixtures of both nanosized and bigger particles. The average size of coarser silica particles was about 10 to 30 μm. Different amounts of tetramethylammoniumhydroxide (TMAH) were added to the suspensions to adjust ζ-potential of the particles suitable for electrophoretic deposition. Rheological behaviour of the suspensions was investigated by means of rotational viscosimetry and ζ-potential of the silica particles was measured by means of a Zeta-Sizer (Malvern). In Addition electrical conductivity and pH were measured to guarantee reproducibility.

Electrophoretic deposition was carried out under constant applied voltage based on the membrane-method[x]. The electrophoresis cell was subdivided into two chambers by an ion-permeable membrane. Two platinum foils were used as electrodes. Suspension was poured into the cathode-sided chamber, water with adequate amounts of TMAH into the anode chamber. Since the membrane used was not permeable for the particles, the deposit was formed at the membrane. In contrast, recombination of ions, generated by the electrolytic decomposition of water at voltages higher than ≈1.5 V, took place at the electrodes. Thus, no formation of gas bubbles was observed within the deposited green bodies. The width of the different chambers was optimised after measuring the effective electric field strength within the electrophoresis cell[xi]. The electric field strength applied were in the range of 1 to 10 V/cm. A deposition time of 0.5 to 10 minutes was chosen. After shaping, the green bodies were dried in air under ambient humidity. No cracking could be observed. Green density of the deposited compacts was determined according to Archimedes method and pore size distribution was measured by mercury porosimetry.

To achieve silica green bodies with graded pore size distribution and porosity and to prepare a silica/metal oxide FGM the electrophoretically deposited green bodies were impregnated with nanosized particles under applied electric field. The experimental set-up for this electrophoretic impregnation corresponded to that of the EPD. The membrane used in case of the EPD was replaced by the open-porous silica green body. Aqueous suspensions of

nanosized powders with comparably low solids content were used. Alternatively, a graded silica/metal structure was achieved by electrolytic impregnation of the porous silica green body. In this case a conducting layer was applied onto one surface of the porous green body. After impregnation the green bodies were dried again and characterised subsequently on the basis of SEM pictures by image analysis and by means of EDX- and optical spectroscopy. Sintering of the compacts was carried out under reducing atmosphere.

Results and discussion

Two routes were pursued for manufacturing of silica glass metal composites by potential-enhanced shaping and subsequent sintering of powders. In every case a porous silica green body was produced and was impregnated electrolytically or electrophoretically with a metal or metal oxide respectively. In the latter case a silica green body with homogeneous density and pore size was prepared by electrophoretic deposition. Mean pore size of the green body was 1.8 µm with and green density was about 65 %TD. An aqueous suspension with 5 wt % tungsten oxide (WO_3) was used to impregnate the green body electrophoretically. Figure 1 shows a SEM image of a fracture surface of such a green composite of silica and tungsten oxide. The surface on contact with the suspension is on the right hand side. A graded change from tungsten oxide to silica was observed. By means of image analysis densification of the green body after impregnation was determined. A densification of 100 % is equated with an amount of about 30 vol. % of tungsten oxide. This means that all the pores of the silica green body were filled with nanosized tungsten oxide particles. This does not mean that theoretical density can be reached, but only that all the larger pores are filled and only nanosized pores in the range of 20 µm exist between the tungsten oxide particles. A shown in figure 1 (drawing) a graded decrease of densification or tungsten oxide was found with increasing distance from surface.

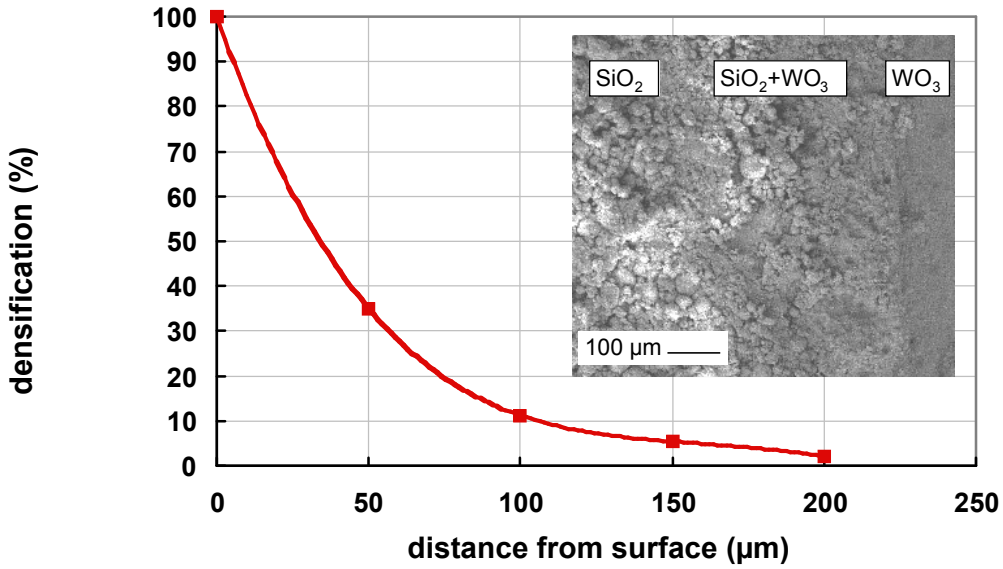

Figure 1: Silica glass tungsten oxide green body with graded chemical composition manufactured by electrophoretic impregnation of a silica green body (left-hand side) and influence of applied electric field on impregnation (right-hand side)

As described before an alternative route to achieve functionally graded silica glass metal composites is the electrolytic impregnation of silica green bodies with graded density and

pore structure. Such silica green bodies can be prepared by electrophoretic deposition via two alternative ways. It could be shown that by adjusting the process parameters (EPD or suspension) during deposition green density and pore size could be tailored. In this work a cast or electrophoretically deposited green body with homogeneous microstructure was impregnated electrophoretically with nanosized particles (Degussa OX50). Thus, a continuous gradient in density and pore size from impregnation surface (contact with suspension) towards bulk of the green body could be achieved. It was shown that steepnes of gradient could be tailored[7] in a wide range and a graded structure of some 10 µm up to several millimetres was achieved. Subsequently, green bodies prepared in such a manner were impregnated electrolytically with copper to show the feasibility of the process. Figure 2 shows a SEM image of silica glass copper green composite with functional decreasing copper content from the upper surface towards the bulk. The black areas are pores of the green body filled with copper. Since melting temperature of copper is to low for these composites to be sintered to full density, in a next test series nickel was deposited within the pores of silica green bodies electrolytically. Figure 3 shows the compositional gradient of a silica glass nickel composite prepared by electrolytic impregnation. Dark and dotted line correspond to green body and sintered composite respectively.

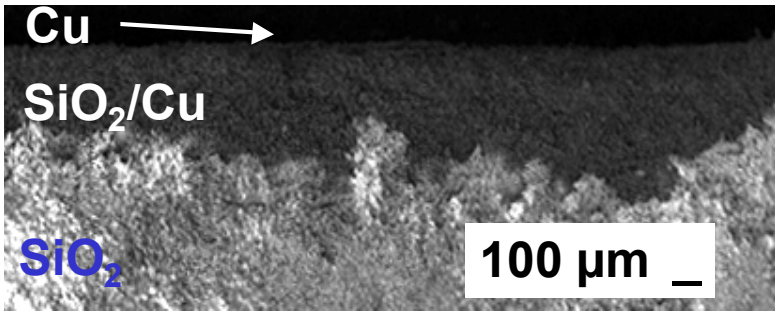

Figure 2: Silica/copper FGM with functionally graded interface by electrolytic impregnation of an electrophoretically deposited silica green body (SEM, fracture surface)

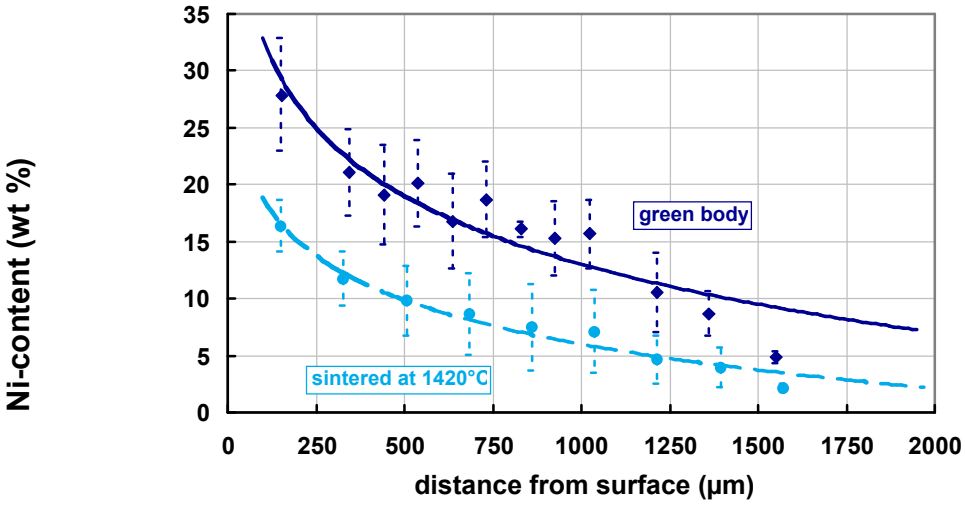

Figure 3: Nickel-content of a functionally graded Ni/silica glass composite (green and sintered) manufactured by electrolytic impregnation of an electrophoretically deposited silica green body

Conclusions

By means of electrophoretic deposition (EPD) of nanosized fumed silica particles and /or coarser silica powders from aqueous suspensions complex shaped silica glass can be manufactured on a competitive scale. Green density and pore size distributions of the green bodies can be tailored by adjusting the parameters of the EPD. Alternatively, silica green bodies with continuously graded pore size distribution and green density could be achieved by electrophoretic impregnation (EPI) of porous silica green bodies with nanosized particles. A functionally graded silica glass/metal or metal oxide green composite could be manufactured by impregnation of such green bodies either electrophoretically (tungsten oxide) or electrolytically (copper, nickel). After sintering under reducing atmosphere a silica glass/metal composite was achieved with continuously graded glass-metal junction.

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